ANALYZING THE RELATIONSHIPS BETWEEN AQUEOUS MANGANESE AND GEOLOGICAL FACTORS IN GROUNDWATER IN THE SHENANDOAH

MARINA CROY, Washington & Lee University
Project Advisor: Margaret A. G. Hinkle

INTRODUCTION

The human health effects of chronic low exposure to Mn greater than 120 ppb have been well documented in recent years (Bouchard et al., 2007; Bouchard et al., 2011). Increased developmental issues in children and infants are correlated with long-term exposure to Mn in areas where Mn was found to be over the EPA limit of 300 ppb (Langley et al., 2015; U.S. EPA, 2004). Numerous other studies have found that chronic exposure to Mn above even the relatively low limit of 100 ppb can be strongly linked to negative health effects, especially in infants and developing children (Bouchard et al., 2011; Bjørklund et al., 2017; Hafeman et al., 2007, Khan et al., 2012; Sanders et al., 2014; Spangler and Spangler, 2009; Spangler and Reid, 2010). The valence state - the ability of the ions of an element to accept or give electrons - largely determines whether Mn will be in the aqueous or solid phase. A lower valence state (found in more anoxic conditions) will result in Mn moving into (or staying in for the case of groundwater) the aqueous phase. A higher valence state will result in Mn(III)/Mn(IV) precipitating out of solution as Mn (oxyhyr)oxides, lowering the concentration of Mn in the aqueous phase. Thus, more reducing systems like groundwater and springs are of particular concern with respect to Mn exposure via low level chronic ingestion of such drinking water sources. Our field work study area consists of four counties across the Shenandoah Valley: Rockbridge, Augusta, Bath and Shenandoah, whereas the analysis for all groundwater wells spanned the entirety of the Shenandoah Valley in Virginia.

METHODS

A total of forty-two 250 mL water samples from the seven different sites was collected across the study area (Fig. 1). Both filtered (0.2 μm) and unfiltered water samples were collected at each site. When applicable, rocks that were characteristic of the site were also collected so that they may be analyzed for metal precipitates. Filtered samples collected in the field were stored in polypropylene centrifuge test tubes, while unfiltered samples were stored in 250-mL polypropylene bottles sealed with parafilm to preserve their contents, and stored in laboratory refrigerators (at 4°C). Upon returning to the lab, coordinates measured in the field were used to determine the underlying geology of the site, which was correlated
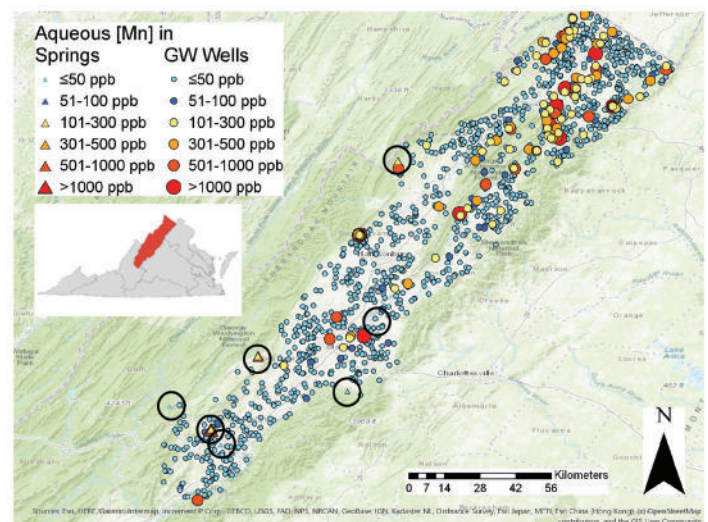

Figure 1. Map of aqueous Mn concentrations in springs (triangles) and groundwater wells (circles) in the Shenandoah Valley, VA, with increasing concentrations increasing the relative size of each data point based on demarcations from ≤50 ppb (light blue) to 51-100 ppb (dark blue) to 101-300 ppb (yellow; above which low level chronic exposure to Mn via drinking water may result in health effects), 301-500 ppb (orange), 501-1000 ppb (light red), to >1000 ppb (dark red). Field sites for springs and seeps are denoted with black circles.

with rock types present at the site. Filtered water samples were diluted by either 1:5 or 1:2 with Milli Q water for analysis by ion chromatography (IC), which analyzed for major ion concentrations (e.g., Ca^{2+}, NO_3^{2-}, SO_4^{2-}, etc.) through IC. The unfiltered, undiluted samples underwent phenolphthalein titration with a bromocresol green-methyl red titration test for $[CaCO_3]$ and $[HCO^{3-}]$. Separate aliquots of filtered spring water samples were acidified to 2% nitric acid (trace metal grade) for analysis via ICP-MS for major and trace elements (e.g., Mn, S, Cr, Fe, Co, Ni, Zn, As, etc.) and diluted with 2% nitric acid in a 1:2 ratio. ICP-MS was performed by the Department of Civil and Environmental Engineering at Virginia Tech. To supplement this research, data from other sources and projects was included in the dataset. Well data, water quality data, and geological map data was obtained from organizations including United States Geological Survey (USGS) National Water Information System (NWIS) and the Virginia Household Water Quality Program (VAHWQP) (McMahon et al., 2018).

RESULTS

ICP-MS analyses found several sites to have aqueous Mn above the 120 ppb limit. Water geochemical analyses also found that some of the samples have high levels of other contaminants (high being defined as concentrations equal to or above safety levels set by the EPA). The drinking standard limits for elements such as lithium (Li), Al, Fe, Mn, and zinc (Zn), were surpassed for several samples, although many of these are considered secondary drinking standards, and thus are not enforceable (Table 1) (U.S. EPA, 2022a,b; Agency for Toxic Substances and Disease Registry (2005), Lindsey et al., 2021).

Interestingly, elevated aqueous Mn concentrations are consistently observed in sandstone and shale aquifers (Fig. 2). Sandstone lithologies exhibit the highest average aqueous Mn in springs and seeps here studied (Fig. 2), along with the largest standard deviation (1σ), with some sites over 500 ppb Mn. Meanwhile, carbonate aquifers have the lowest average aqueous Mn concentrations, with the average and standard deviation below the 100 ppb threshold for chronic exposure health concerns (Fig. 2). The decrease in aqueous Mn in carbonate aquifers may be due the fact

Table 1: Table featuring the EPA secondary drinking standard limits for elements other than Mn analyzed in ICP-MS, as well as any samples with concentrations above the limits.

SampleID	$[Li]_{aq}$ ppb	$[Al]_{aq}$ ppb	$[Fe]_{aq}$ ppb	$[Mn]_{aq}$ ppb	$[Zn]_{aq}$ ppb
EPA drinking water limit (ppb)	10	200	300	300	5000
Rockbridge Pond Spring-01	--	--	467.5	1,321.6	--
Rockbridge Pond Spring-02	--	--	--	172.7	--
Rockbridge Pond Spring-03	--	--	--	341.5	--
Augusta Country Spring Complex-01aa	--	--	1,011.4	555.0	--
Augusta Country Spring Complex-02	--	--	240.3	238.1	--
Shenandoah County Pump Spring-01	--	--	14,339.5	155.3	34,474.7
Shenandoah County Pump Spring-02	--	--	2,479.0	--	--
Shenandoah County Pump Spring-03	--	201.2	1,827.3	--	--
Orkney Spring	12.8	425.8	6,093.8	--	--
Orkney Spring A	13.4	412.8	5,394.5	--	--
Orkney Spring B	13.0	284.3	3,923.9	--	--
Shenandoah County Meadow Spring-01	77.1	--	28,442.0	228.8	16,735.9
Shenandoah County Meadow Spring-02	78.8	296.9	14,567.9	191.7	--

these are weathered carbonates contributing to the karst terrain in the region, thus exhibiting substantial surface water-groundwater connectivity, therefore are likely more oxic, making Mn more stable as Mn oxide minerals (Fig. 3A). Alternatively, carbonate bearing aquifers could have increased bicarbonate concentrations, thereby stabilizing Mn^{2+} in Mn carbonate minerals such as rhodochrosite (Fig. 3B).

Aqueous Mn concentrations exhibit consistently negative correlations with pH and dissolved oxygen (Fig. 4). However, it should be noted that depending on the lithology these correlations can be quite weak (with relatively low R^2 values), albeit the trends are consistent (Fig. 4). Given the nature of Mn thermodynamic stability as it relates to pH and
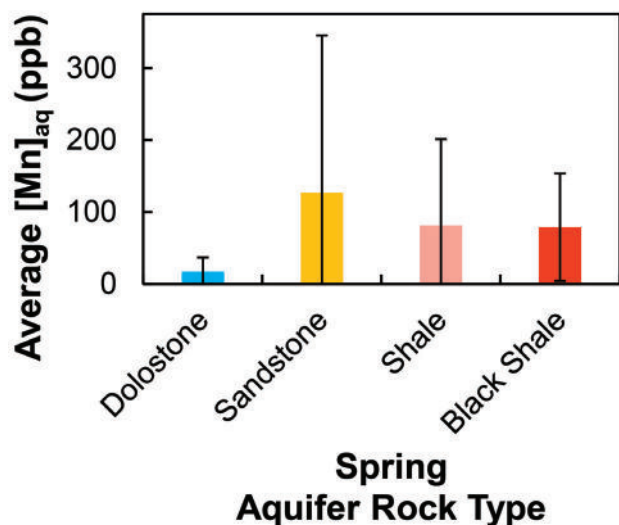
Figure 2. Average [Mn] within each aquifer lithology designated by the primary rock type within the corresponding lithologic unit, with black bars denoting standard deviation of 1σ.
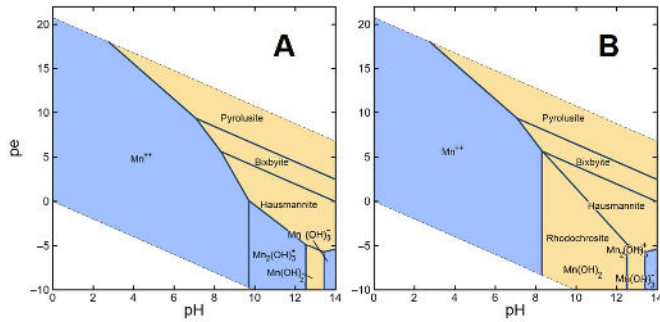
Figure 3. pe/pH diagrams using average [Mn]aq (0.19 ppm) & pH (6.3) of sampled spring sites, with no HCO3- (A) & average [HCO3-]aq from spring sites (56.45 mg/L) (B). Made with Geochemist's Workbench..

reduction potential, with Mn stable as aqueous Mn^{2+} under acidic and reducing conditions (Fig. 3), these negative correlations between Mn and pH and Mn and dissolved oxygen are consistent with its expected behavior. Interestingly, and consistent with the concept that bicarbonate will stabilize Mn in the solid phase in Mn carbonate minerals, all rock types exhibit slightly negative correlations between Mn and alkalinity, although the R^2 values for these are quite low (Fig. 4C).

The lithologic trends continue when examining correlations between aqueous Mn and other trace metals and major elements. Fe, as expected, was found to be strongly positively strongly correlated with Mn in all aquifers, but only when separated out by lithology. The R^2 value for Mn and Fe in sandstone aquifers is 0.93, in black shale aquifers is 0.85, and in carbonate aquifers is 0.42 (Fig. 4F). It should be noted that Fe concentrations in the black shale aquifers are, on average, much higher than Fe concentrations in other aquifers (Fig. 4F). Co also exhibits a similar trend (with R^2 values quite similar to those for Mn and Fe), and thus may demonstrate that aqueous Co concentrations are dependent on Fe, Mn, or some combination thereof (Fig. 4H). In black shale and sandstone aquifers, Mn is positively correlated with S, Co, and Ni (Fig. 4). Mn is negatively correlated with As in black shale aquifers but is positively correlated in sandstone and carbonate aquifers (Fig. 4L).

DISCUSSION

Lithology appears to have a major influence on the geochemistry of springs, due to the effect of sulfur and dissolved organic carbon in redox geochemistry as
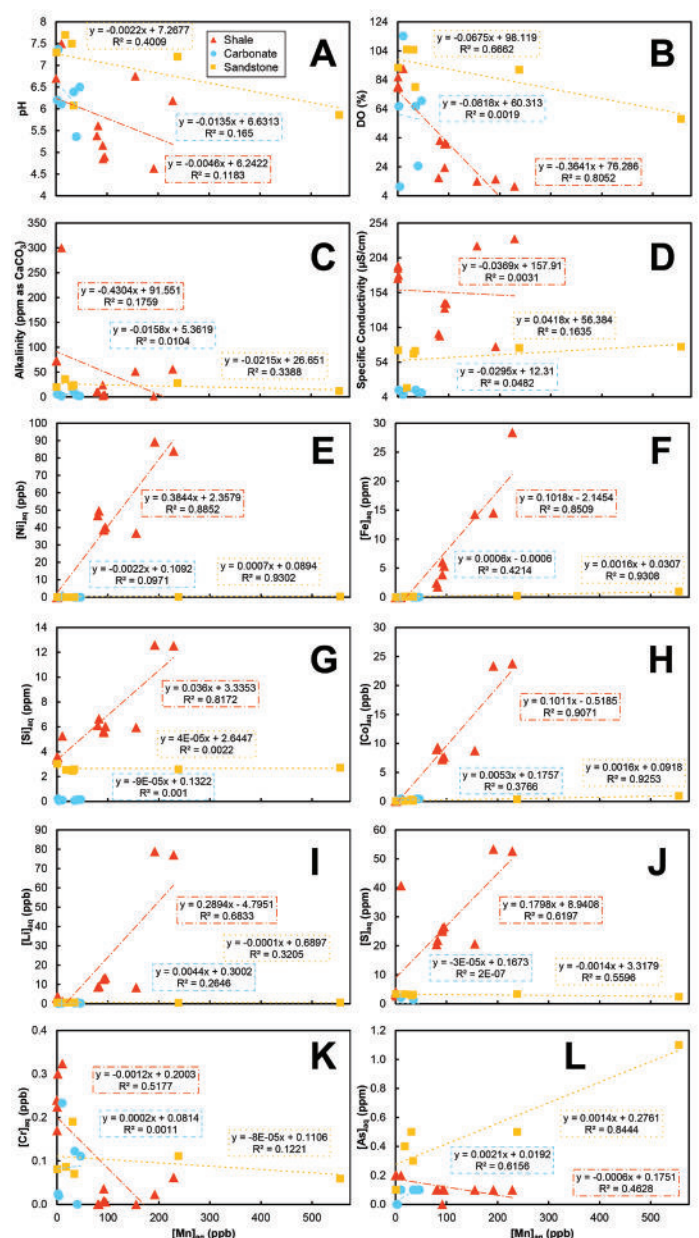

Figure 4. Aqueous [Mn] versus various field parameters: pH (A), dissolved oxygen (B), alkalinity (C), specific conductivity (D), and elements of interest in the aqueous phase: Ni (E), Fe (F), Si (G), Co (H), Li (I), S (J), Cr (K), As (L) separated by aquifer primary rock types with sandstones (orange squares), shales (red triangles), and carbonates (blue circles).

well as the more oxic nature of weathered carbonate aquifers. The presence of sulfides in black shales shifts the reduction potential such that the Mn present in shale aquifers is most stable in a lower valence state (II), which is soluble and results in the Mn staying within the aqueous phase as opposed to entering a higher valence state (III/IV) and precipitating into a solid form, thereby decreasing aqueous Mn(II) concentrations (Fig. 2). In the graph of [S] vs [Mn], the trend of increasing S and increasing Mn in black

shales is an example of this process (Fig. 4). Fe can be used to track the reducing conditions in aquifers, with a suggested threshold of 100 ppb Fe resulting in more anoxic aquifers (Erickson et al., 2019). The black shale aquifers in this study consistently have Fe concentrations above the 100 ppb threshold for anoxic conditions, while carbonate bearing aquifers have much lower Fe concentrations, suggesting that carbonate aquifers are more oxic than black shales in this region. The sulfur-bearing black-shales that create reducing conditions, which cause the Mn to persist in a lower valence state, thus keeping Mn in the aqueous phase, have similar effects on aqueous Fe.

CONCLUSION

Our data indicates that lithology is a major factor affecting groundwater chemistry in the Shenandoah Valley, particularly with regard to the distribution of Mn. The lithology of an aquifer will impact the geochemistry of the water that is stored within it, specifically the redox geochemistry, which will result in a change in the transfer of the electrons and the valence state of elements such as Mn. Thus, it is clear that there is a defined set of cause-and-effects that can be traced in defining where Mn is located (the solid or aqueous phase) where it is likely to move, depending on geochemical and environmental factors. To sum up, aquifer lithology affects the geochemistry within the aquifer, which affects the Mn valence state, which affects the movement of Mn into different phases and forms. Trace metals may bind onto the Mn oxides via sorption processes, resulting in high concentrations of these elements associated with Mn oxides, but may also be released to solution when exposed to reducing conditions with Mn oxide dissolution to aqueous Mn(II). Mn oxides are known as the "scavengers of the sea" due to their highly sorptive properties, as they are able to manipulate the distribution of a range of elements (Tebo et al., 2004). Since Mn(II) is thermodynamically favored in anoxic conditions, and Mn(III)/(IV) are favored in oxic conditions, the state of Mn and presence of Mn oxides can be predicted in groundwater aquifers based on DO. Mn oxides can absorb many different types of ions, and as a result, Mn oxides can control the concentrations of trace metals in natural waters, also allowing the correlation of Mn and elements such as Fe and arsenic (Tebo et al., 2004).

Overall, Mn is an invaluable resource in predicting the mobilization and concentrations of trace elements in groundwater, similar to how Fe can be used to signify reducing or oxidizing conditions. Fe, Si, Ni, Li, S, and Co all have strong positive correlations with Mn, meaning that their concentrations could possibly be predicted in areas where the concentration of Mn is already established. However, due to the close correlation between Fe and Mn, Fe may be as much of a control as Mn on trace metals of interest, and future work may decipher how much each of these two elements plays a role in controlling geochemistry. Future work may also attempt to create a model that can appropriately predict and measure the amount of certain trace metals in an aquifer based on the Mn concentration, or other common water quality measurements such as DO and pH.

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